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13. ABSTRACT (Maximum 200 words)  Initial investigations of polymer electrolytes based on PVdF-HFP and LiPF <sub>6</sub> dissolved in either EC/PC or EC/DMC mixtures have been carried out via high pressure complex impedance methods and <sup>7</sup> Li NMR. All results indicate that the polymer matrix, while effectively immobilizing the liquid component, does not significantly affect the ion transport mechanism inherent to liquid electrolytes. In the first reported attempt to exploit <sup>17</sup> O NMR to study lithium battery electrolytes, we have prepared <sup>17</sup> O-enriched Li triflate and several electrolytes containing the isotopically enriched salt dissolved in DEC, DMC, and mixtures of DMC/EC. Line widths were measured as a function of electrolyte solvent and temperature, and suggest that EC inhibits the formation of ion pairs, when added to DMC.				
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*Lithium Ion Transport Across and Between Phase Boundaries in  
Heterogeneous Polymer Electrolytes Based on PVdF*

FINAL PROGRESS REPORT

Steven G. Greenbaum

February 26, 1998

U.S. ARMY COMMUNICATIONS AND ELECTRONICS COMMAND,  
jointly with U.S. ARMY RESEARCH OFFICE

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## **Final Progress Report**

### *Lithium Ion Transport Across and Between Phase Boundaries in Heterogeneous Polymer Electrolytes Based on PVdF*

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5. AUTHOR OF REPORT: Steven G. Greenbaum, Professor of Physics
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accepted for presentation at the 8<sup>th</sup> International Meeting on Lithium Batteries, Scotland, July,  
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8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT:
  - a) Dr. Telitha Murray, postdoctoral associate
  - b) Ms. Sophia Suarez-Gustave, MA degree candidate (most of her support came from College  
and other sources).
9. REPORT OF INVENTIONS: None

## Technical Description

### Specific aims -

A great deal of effort, world-wide, is being spent on the development of gel electrolytes based on poly(vinylidene difluoride) (PVdF). These materials appear to offer the requisite dimensional stability without seriously compromising ionic conductivity. A key requirement of these electrolytes is that they must be homogeneous because, otherwise, long-range ion transport could be impeded at phase boundaries. In previous work published by our group prior to receiving this grant, it was demonstrated that the addition of about 10 wt% nanoscale  $\text{TiO}_2$  could have a large effect on suppressing phase boundaries. It is interesting to note that high surface area inorganic oxides such as  $\text{Al}_2\text{O}_3$  and fumed silica are routinely added to the plasticized polymer prior to injecting the liquid electrolyte, in order to prevent collapse of the film while the plasticizer is removed. Little attention has been given (at least in the published literature) to the effect of the inorganic oxide additives on *electrical* properties. Our efforts are focused on correlating short-range ionic motion, as probed by NMR, with long-range ion transport. A second research activity undertaken was to explore the possible use of oxygen-17 NMR as an alternative (to vibrational spectroscopy) tool to investigate ion-ion interactions in liquid and polymer electrolytes.

### Results -

#### PVdF-electrolytes

In a joint study with long-time collaborators John Fontanella and Phil Stallworth of the U.S. Naval Academy, and also with Tony Gozdz of Bellcore, electrical conductivity and NMR studies have been carried out on liquid electrolytes such as EC:PC and EC:DMC containing  $\text{LiPF}_6$  and polymer films plasticized using the same liquid electrolytes. The polymer films are (PVdF) copolymerized with hexafluoropropylene (HFP). Complex impedance studies were made at frequencies from 10 Hz to 100 MHz at pressures up to 0.3 GPa (3 kbar) at room temperature. In addition, studies were carried out in vacuum at temperatures down to 5.5K. Significant differences between the EC:PC and EC:DMC liquid electrolytes are found. In addition, the behavior of the plasticized polymer films was compared with the response of the corresponding liquid electrolytes. The variable pressure measurements yield activation volumes for ion transport. The values in the polymer electrolytes are close to those found in the corresponding liquids, indicating that liquid-like conductivity occurs in the PVdF-based electrolyte. By contrast, earlier work by our research group on poly(acrylonitrile) (PAN) - based gels found a difference in activation volumes between the gels and liquid electrolytes, indicating that the polymer matrix interacts strongly with the ions. Lithium-7 NMR relaxation time measurements were utilized to determine ionic motional correlation times in PVdF-electrolytes. Again, these were close to the values obtained for the corresponding liquid electrolytes.

#### Oxygen-17 NMR

Because the natural abundance of  $^{17}\text{O}$  is quite low, isotopic enrichment of electrolyte salts

has potential applications in the investigation of liquid, and eventually, polymer electrolytes. Our investigation was a first attempt to exploit  $^{17}\text{O}$  NMR as probe of ion-solvent and ion-ion interactions in lithium battery electrolytes. A novel approach to the synthesis of  $^{17}\text{O}$ -enriched lithium triflate ( $\text{CF}_3\text{SO}_3\text{Li}$ ) was undertaken. The  $^{17}\text{O}$  spectra of the enriched salt in a number of solvents, DMC - dimethylcarbonate, DEC - diethylcarbonate and mixtures of DMC and EC - ethylenecarbonate, were then compared. Spectra of solvent oxygens, at natural  $^{17}\text{O}$  abundance, were also obtained. Evidence for solvent-separated ion pairs or aggregates was postulated from the C=O and sulfonate  $^{17}\text{O}$  NMR line widths, for which the DMC/EC 1:1 electrolyte exhibits the lowest and least temperature-sensitive values. It would be of interest in future investigations to explore the salt concentration dependence of both chemical shift and line width. It would also be of interest to examine electrolytes prepared with Li salts with other oxygen-containing anions that are more soluble than Li triflate.